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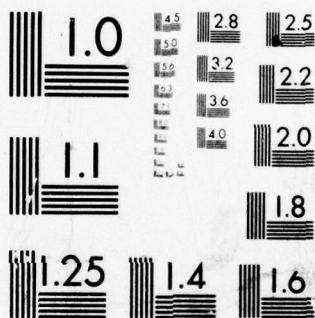
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Flexible polymers from conjugated organic ligands and nonrigid metal
centers have been synthesized and have been evaluated for thermal stability.
A tungsten polymer, bis(5,7-dichloro-8-quinolinolato)-5,8-quinoxalinediolato-
tungsten(IV) with number average molecular weight near 40,000 to 50,000
Daltons has been synthesized from the quinoxalinedione and a tungsten(II)
intermediate. Several other polymers, monomers, and intermediates have also
been investigated, where the metals range from molybdenum and tungsten to

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Zirconium and the eight-coordinate centers are all N_2O_4 ligand donor sets, and with the seven-coordinate intermediate possessing carbon, phosphorus, nitrogen, oxygen, and/or chlorine donors. The molybdenum and tungsten species appear to have energy-transfer potential.

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FLEXIBLE METAL CHELATE POLYMERS THROUGH
NONRIGID METAL CENTERS

FINAL REPORT

Ronald D. Archer
Principal Investigator

May 30, 1979

U. S. ARMY RESEARCH OFFICE

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TABLE OF CONTENTS

	<u>Page</u>
Table of Contents	2
List of Manuscripts	3
List of Personnel Supported	4
Problem Studied	5
Summary of Results	5
Bibliography.	7
Appendix: Abstracts of papers in Press	8

LIST OF MANUSCRIPTS

1. Archer, R.D.; Donahue, C.J., "Nonrigidity in Eight-Coordinate Tetrakis Chelates: The Stereochemical Integrity and Geometrical Isomerism of Tungsten(IV)(methylpicolinato)_n(5,7-dichloro-8-quinolinolato)_{4-n} Complexes", J. Am. Chem. Soc., 1977, 99, 269-71.
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11. Day, R.O.; Batschelet, W.H.; Archer, R.D., "The Molecular Structure of Three Seven-Coordinate Tungsten(II) Chelates with Hard and Soft Donors", manuscript in preparation.

PERSONNEL SUPPORTED & DEGREES AWARDED

Graduate Students

Craig J. Donahue, Ph.D., January 1977 [Asst. Prof., U. Mich., effective, Fall 1979]*

Marvin L. Illingsworth, Ph.D. in progress (estimated date: August 1979)**

Carl J. Weber, Ph.D. in progress (estimated date: January 1981)**

Postdoctoral Associates

David R. Whitcomb, 1 year [3 M - Research]

Craig J. Donahue, 1 year after Ph.D. (1/2 research & 1/2 teaching) [See above]

David J. Kowalski, 2 months [Nalco - Research]

William H. Batschelet, 1 1/2 years **

Douglas W. Hensley, 8 months (1/2 research & 1/2 teaching)**

Undergraduate Assistants

Paul Palumbo (graduate school)

Christopher Hardiman**

Brian Devine**

The Principal Investigator took partial summer support (3 summers). Professor C. P. Lillya received one week summer support for his help in the organic synthesis and supervision of Mr. Palumbo and Dr. Kowalski.

* Positions of professionals who have left UMass.

** Still at UMass.

PROBLEM STUDIED

Polymerization studies involving nonrigid, but substitution-inert, metal ions were proposed with d^2 eight-coordinate complexes of molybdenum(IV) and tungsten(IV) as the prime candidates. The rationale for the studies have been based on the observation that the thermal stability of inorganic polymeric systems has normally been sacrificed to obtain plasticity through the introduction of less thermally stable organic groups which exhibit free rotation. Nonrigid centers should allow plasticity without the addition of thermally weaker but flexible organic chains.

The primary goal was to form linear polymers with chelating bridging ligands with the concurrent use of blocking ligands in some of the coordination positions. The research plan consisted of (1) an initial phase to evaluate the nonrigidity of inert chelated eight-coordinate species with nonequivalent donors. (2) The synthesis of bridging ligands such as 5,8-quinoxalinediol, bis(8-hydroxy-5-quinolyl)-methane, 4,4'-bipyridyl-2,2'-dicarboxylic acid, and 4,7-phenanthroline-5,6-diol were projected to supplement the commercially available pyrazine-2,3-dicarboxylic acid. (3) The synthesis of eight-coordinate polymers was proposed via seven-coordinate intermediates, after synthesis of the latter had been accomplished. (4) The synthesis of a seven-coordinate polymer (followed by stabilization as an eight-coordinate polymer), brute-force polymerization, and/or substitution polymerization were projected as possible experimental approaches, but were deemed less likely modes for successful polymerization. (5) Extension of the studies to polymers with zirconium(IV), which is more labile but still eight-coordinate, and to polymers with rigid coordination-sphere metals was projected as further aspects of evaluating the results with the eight-coordinate species. (6) Finally, physical and chemical studies of the polymers were projected.

SUMMARY OF RESULTS

We met our primary and related goals as briefly outlined below.

(1) Our initial goal of evaluating the non-rigidity of inert eight-coordinate chelates with four nitrogen and four oxygen donors have been shown to be pseudo-rigid.¹⁻³ This means that although free rotation is precluded, flexibility is still possible.

(2) Numerous bridging ligands were synthesized and evaluated. To maintain aromaticity without weak links, an emphasis on 5,8-quinoxalinediol as a bridging ligand developed. This was followed by 1,5-naphthyridine-4,8-diol in order to avoid two nitrogens in the same ring (which provides low nucleophilicity) and the thermally weak external carboxylates of other logical sources. 4,7-Phenanthroline-5,6-diol which avoids these problems (but has alternate chelation possibilities) and the dimer of pyridine-2-aldehyde were also investigated as bridging possibilities. Three of them, the quinoxalinediol, the phenanthrolinediol, and the pyridine-aldehyde dimer have an oxidized dione form suitable for two electron reduction as a metal is oxidized by the same amount. The synthesis and solubility problems surrounding naphthyridinediol precluded its extensive use until late in the project.

(3) Seven-coordinate intermediates were synthesized.⁴ This phase of the study caused considerable delay in the remainder of the project because compounds such as $W(CO)_3(8\text{-quinolinol})_2$ were too sensitive to prepare in adequate purity. Eventually $W(CO)_2(PPh_3)(8\text{-quinolinol})_2$ type species were prepared as suitable intermediates for the subsequent parts of the study. The molecular structure of the desired intermediate was refined and found to be seven-coordinate⁵ as predicted.⁴ Other seven-coordinate intermediates were noted in progress report 5.

The synthesis of a polymeric tungsten(IV) chelate from a seven-coordinate intermediate and the quinone form of the quinoxalinediol ligand was a success.⁶ Inherent viscosities of up to 0.25 have been obtained from the dimethylsulfoxide fraction. Unfortunately, the low nucleophilicity of the ligand precludes extreme thermal or long term solution stability. The ability of the tungsten(II) chelate and the quinone to provide a tungsten(IV) polymer is a very significant finding. Studies with other bridging ligands were in progress at the termination of the grant.

(4) One seven-coordinate tungsten(II) polymer was synthesized and attempts were made to oxidize it to an analogous eight-coordinate tungsten(IV) species. As anticipated, this method appears less promising. We were in the process of developing the substitution polymerizations at the termination of the grant, but brute-force polymerizations were avoided.

(5) Extension to zirconium was pursued, primarily through related Materials Research Laboratory support, and oligomers with intrinsic viscosities of up to 0.15 for unfractionated materials have been obtained.⁶ With zirconium, double-headed bis-quadridentate Schiff-base ligands were used to minimize the lability effects.

(6) The characterization of the polymers at their current state of oligomerization has involved chemical analysis, viscosity measurements in dimethylsulfoxide, spectral characterizations (vibrational and electronic), and thermal analysis.⁶ The viscosities are indicative of number average molecular weights of 40,000 to 50,000 for the tungsten polymer and 20,000 for the zirconium polymer. The chemical analysis for the zirconium polymer suggests an even higher molecular weight value. The spectral properties are all consistent with linear polymers and the higher molecular weight fractions form glasses and films. The thermal properties have indicated a slight decomposition, apparently through the interaction of moisture or solvated dimethylsulfoxide near 250°C, with major decomposition near 400° and 510°C for the zirconium and tungsten polymers, respectively, in air. Full details are to be published.⁶

(7) Furthermore, in order to ascertain the best approaches to the polymer syntheses a reasonable amount of effort was spent completing work with some of the model eight-coordinate monomers including the synthesis and characterization of several new molybdenum(IV),⁷ tungsten(IV),⁸ and zirconium(IV)⁹ chelates. During the course of the investigation it became apparent that these chelates are photochemically active and that the polymers may have energy-transfer potential.¹⁰

Scaled-down polymerization studies are continuing at the present time thanks to the support of the NSF/MRL program.

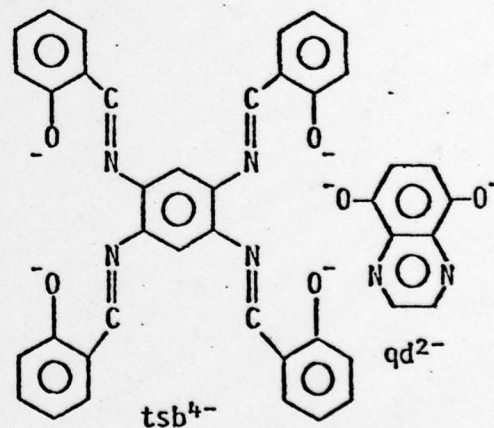
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2. Manuscript No. 2
3. Manuscript No. 6
4. Manuscript No. 8
5. Manuscript No. 11
6. Manuscript No. 9
7. Manuscripts No. 5 and 10
8. Manuscript No. 3
9. Manuscript No. 4
10. Manuscript No. 7

LINEAR CONJUGATED COORDINATION POLYMERS CONTAINING EIGHT-COORDINATE ZIRCONIUM AND TUNGSTEN. Ronald D. Archer, William H. Batschelet and Marvin L. Illingsworth.
Department of Chemistry, University of Massachusetts, Amherst, MA 01003

Flexible polymers from conjugated organic ligands and nonrigid metal centers are being synthesized and evaluated for thermal stability and energy transfer potential. Eight-coordinate zirconium and tungsten are parts of 1,2,4,5-tetrasalicylidene-tetraamino-benzenatozirconium(IV), $[\text{Zr}(\text{tsb})]_n$, and bis(5,7-dichloro-8-quinolinolato)-5,8-quinoxalinediolato-tungsten(IV), $[\text{W}(\text{dcq})_2(\text{qd})]_n$, respectively.

The zirconium polymer was synthesized from the salicylaldehyde chelate of zirconium and tetra-aminobenzene in dry dimethylsulfoxide. The polymer is thermally stable to about 350°C in air. The tungsten polymer has been synthesized from the qd quinone oxidation of $\text{W}^{\text{II}}(\text{CO})_2(\text{PPh}_3)(\text{dcq})_2$. Whereas thermal decomposition begins at a lower temperature, the final step in air to WO_3 occurs above 500°C. The energy transfer potential of the latter class of polymers will also be discussed. The bridging ligand in the two polymers are:



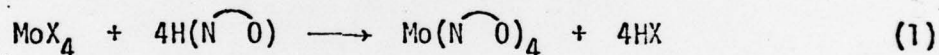
Proceedings Third International Conference on the
Chemistry and Uses of Molybdenum, Ann Arbor, Michigan,
August, 1979, In Press.

EIGHT-COORDINATE MOLYBDENUM CHELATES

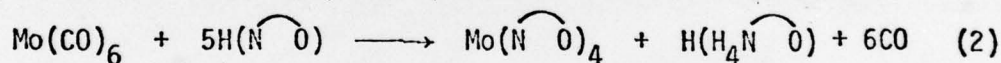
Ronald D. Archer,* Carl J. Weber and Craig J. Donahue¹
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ABSTRACT

Although $\text{Mo}(\text{CN})_8^{4-,3-}$ salts have long been known, stable eight-coordinate chelates of molybdenum have only recently been prepared. In addition to the previously known $\text{Mo}(\text{S} \curvearrowright \text{S})_4$ type species, we have isolated chelates with $\text{Mo}(\text{N} \curvearrowright \text{O})_4$ type donors, where the nitrogen donors are unsaturated heterocyclic donors, such as the picolinate (pic^-) anion. Approaches to the synthesis of such species have included metathesis and redox methods. Schematically,



and



where X = amide or halide and $\text{H}(\text{H}_4\text{N} \curvearrowright \text{O})$ is the tetrahydro reduced form of an aromatic heterocyclic ligand, $\text{H}(\text{N} \curvearrowright \text{O})$, like picolinic acid or 8-quinolinol. Insoluble intermediate chelates often preclude the first method. We have studied the chemical, spectral and magnetic properties of representative chelates and have produced chelates with more than one chelating ligand.